DEFENCE RESEARCH BOARD OF CANADA

IN ASSOCIATION WITH

DEPARTMENT OF MECHANICAL ENGINEERING

UNIVERSITY OF TORONTO

# THE OXIDATION, DECOMPOSITION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

## XXX. THE ROLE OF NUCLEI IN THE IGNITION BY COMPRESSION OF GASEOUS HEPTANE-AIR MIXTURES: FIRST PAPER

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# THE OXIDATION, DECOMPOSITION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

## XXIX. THE ROLE OF NUCLEI IN THE IGNITION BY COMPRESSION OF GASEOUS HEPTANE–AIR MIXTURES: FIRST PAPER[1]

By R. O. King[2] and A. B. Allan[3]


### ABSTRACT

The temperature of a special plug protruding into the combustion chamber of a C.F.R. carburetor engine was adjustable to provide a surface at temperatures higher, lower, or equal to that of the exhaust valve whether it was uncooled or sodium cooled. Compression ratio was always adjusted for maximum power output. This optimum value varied with the temperature of the exhaust valve as well as with mixture strength. These factors are dependent variables. The experimental results support the view that mixtures richer than 25% weak were ignited by nuclei of finely divided carbon derived from pyrolysis of the heptane and that the inflammability of the nuclei increased over the mixture range 25% to 40% weak owing to their absorption of aldehydes. The rate of formation of aldehydes increased as mixture strength was further reduced and it appears that nuclei of ignition then became resinous substances, formed of the condensation products. Further experiments with weak mixtures are to be described in a second paper on the subject of this Part.


### INTRODUCTION

Hydrogen in mixtures with air was used as the fuel for experiments with a C.F.R. engine described in Part XXVII (7) and ignition by compression did not occur even at values of compression ratio rising to 12:1 unless nuclei of finely divided carbon were provided by the decomposition of lubricating oil vapor.

Paraffin fuels differ from hydrogen in that they provide nuclei of ignition at values of the compression ratio which, if speed is constant, depend mainly on the factors of mixture strength and the temperature attained by the exhaust valve. Experiments carried out with the C.F.R. engine in the conditions required to determine the effect of these factors are described in this Part. The fuel used was heptane as supplied by Phillips Petroleum Company for the ASTM method of knock rating. Operating conditions were as adopted for the experiments with acetaldehyde and diethyl ether Part XX (2), and the subsequent experiments with heptane, hexane, and pentane, Part XXI (6) and Part XXIV (3), namely: engine speed 400 r.p.m., air supply temperature 50° F.; engine coolant water 100° F. at the outlet from the cylinder head jacket and approximately 97° F. at the entrance to the jacket of the cylinder barrel; a subnormal charge density, 64% of normal was used.

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[3]*Scientific Officer, Defence Research Board.*





### I. EXPERIMENTAL ARRANGEMENTS

The standard shrouded inlet valve of the engine was replaced by an exhaust valve in order to eliminate a swirl in the mixture entering the cylinder. The engine was direct connected to a d-c. generator arranged as a swinging field dynamometer. Speed was maintained at 400 r.p.m. by adjustment of load.

The air supply was refrigerated to remove excess moisture in order to avoid ice formation in the carburetor. The temperature of the air was then raised to 50° F. prior to its supply to the carburetor. Engine cooling was by a thermostatically controlled water circulation.

The subnormal charge density was used in order to enable the engine to tolerate the degree of detonation caused by the compression ignition of mixtures richer than 25% weak. It was obtained by fitting a choke tube to the standard C.F.R. carburetor, as described in Part XIX (5, pp. 31 and 40). The choke tube required for a reduction of charge density to 64% of normal was $\frac{1}{4}$ in. only in inside diameter because of the low engine speed of 400 r.p.m. The pressure in the choke tube during the induction stroke was found by a separate experiment to be approximately half an atmosphere. Vaporization of the fuel was promoted accordingly and further by the heat of compression, by that of the residual gas, and by heat absorbed from hot surfaces in the combustion chamber.

Abbreviations used in subsequent text are: C.R. for compression ratio, M.S. for mixture strength, I.T.E. for indicated thermal efficiency, and t.d.c. for top dead center. Stoichiometric mixtures are described as "correct" in the text and as C.C.M. on graphs. Mixture strength is described as per cent weak or rich according to the percentage by which the concentration of fuel in the mixture with air is less or more than is required for a correct mixture.

### II. METHOD OF EXPERIMENT

The method was based on the use of the "temperature plug" illustrated by Fig. 1. This device will be described as a "T.P". It was of mild steel machined from solid stock and contained an air cooling device and the leads to a thermocouple for the measurement of the temperature of the rounded end, which protruded slightly into the combustion chamber. The temperature attained by that end when not cooled was from 300° to 400° F. higher than that of the exhaust valve, depending on the variation of heat load with mixture strength. Cooling air was supplied from a high pressure source and provision was made for regulation of the flow in a manner to maintain the temperature of the rounded end at any particular value lower than that attained when it was not cooled.

The C.R. required for ignition was always adjusted to the value at which maximum combustion pressure occurred at the time necessary for the development of maximum power output. This time, taken in degrees of crank angle, varied little from 10° after t.d.c. The corresponding C.R. is the optimum value and is described in subsequent text as the Opt. C.R. Thus the end of the "delay period" required for nuclear ignition was fixed and consequently the

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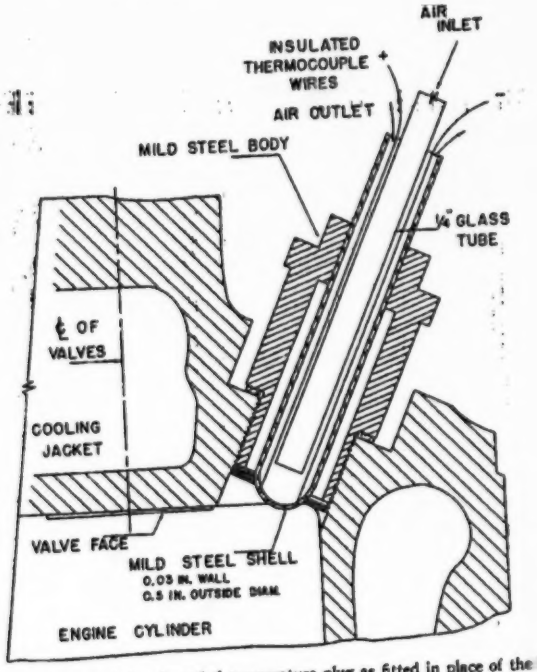


FIG. 1. Illustration of the air-cooled temperature plug as fitted in place of the bouncing pin.

values obtained for I.H.P. and I.T.E. were always consistent with particular values of M.S.

*Preliminary Experiments*

These were carried out in order to illustrate by indicator diagrams the method of using the T.P. Heptane was used as the fuel and the mixture with air was adjusted to be nearly correct; as measured it was 2.3% weak. Pressure–time and rate of pressure change diagrams were taken simultaneously by a Dumont dual beam oscilloscope. The cylinder was provided with three spark plug holes in the wall. One was used for a "Sunbury" magnetic flux pressure pickup to obtain rate of pressure change diagrams. A "Photocon" capacitance type pickup was used in another hole to obtain pressure–time diagrams. The third hole was fitted with a mild steel blank plug. Timing blips were fed into the electronic circuit at t.d.c. and at 10° intervals before and after. The blips

PLATE I

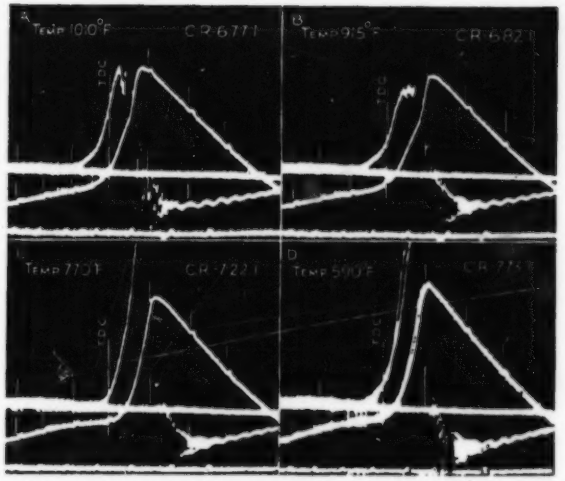


FIG. 2. Pressure–time and rate of pressure change diagrams taken simultaneously to show the increase in the Opt. C.R. at which ignition occurs as plug temperature is reduced to be equal to or less than that of the exhaust valve, nearly correct heptane–air mixtures.

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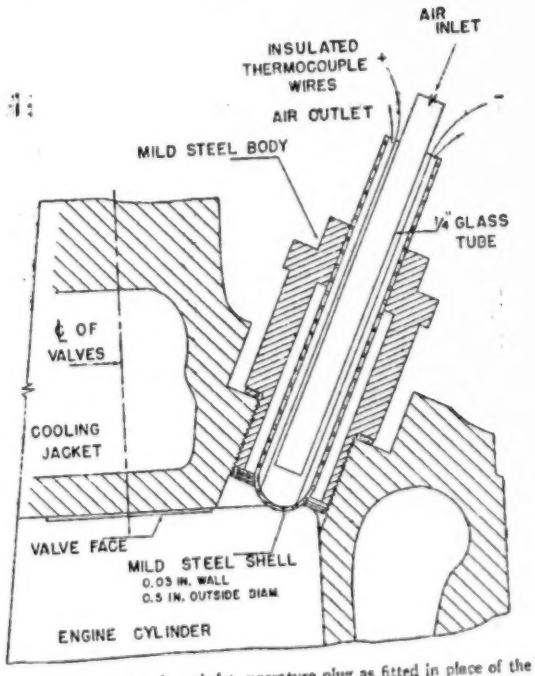


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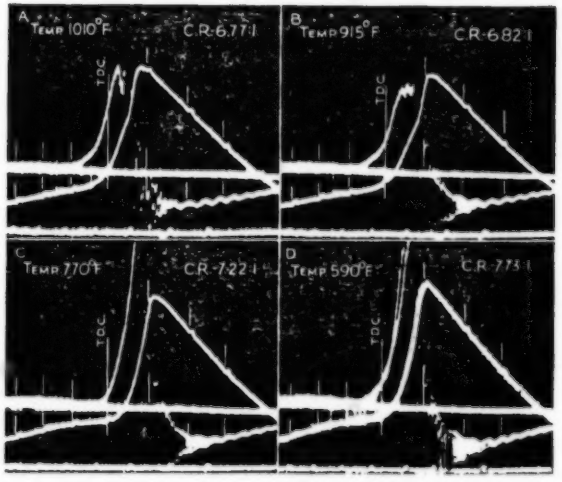


FIG. 2. Pressure–time and rate of pressure change diagrams taken simultaneously to show the increase in the Opt. C.R. at which ignition occurs as plug temperature is reduced to be equal to or less than that of the exhaust valve, nearly correct heptane–air mixtures.

are not always plainly visible on the photographic copies of the diagrams and short vertical lines have been added to mark their positions.

Four of the double diagrams taken during the experiments are reproduced as Fig. 2 and numbered A to D.

*A Diagrams*

These were taken with the T.P. uncooled. It then attained a temperature of 1010° F. and the Opt. C.R. was 6.77. It is shown by the pressure–time diagram that maximum combustion pressure occurred at 8° after t.d.c. and it is evident from the initially low rate of pressure rise that combustion was initiated by surface ignition. However, before it was completed by the normal thermal process of flame propagation, nuclear ignition accompanied by detonation occurred in the mixture ahead of the flame front (the end gas) and combustion was completed in 2° of crank revolution. Thus detonation was a consequence of nuclear ignition of the end gas.

*B Diagrams*

The T.P. was cooled to 915° F. A small increase of C.R. to 6.82 only was then required in order to obtain the optimum value. The characteristics of combustion were as described in respect of the A diagrams. The occurrence of both maximum combustion pressure and nuclear ignition about 4° of crank revolution later than shown by the No. 1 diagrams is without significance because it represents the variation that may occur in successive cycles.

*C Diagrams*

The T.P. was cooled to 770° F. and the Opt.C.R. then became 7.22. Both diagrams show that the T.P. ceased to initiate surface ignition when its temperature had been reduced to 770° F. The rate of heat liberation by the oxidation reaction proceeding on its surface was then too low to raise the adjacent mixture to the temperature required for an igniting effect. The ignition that did occur is attributed to the nuclei formed during compression. The absorption of heat by the decomposition reaction accounts in part for the failure of compression pressure to rise in the normal manner during the latter part of the compression stroke, as is shown by the rate of pressure change diagram.

*D Diagrams*

The T.P. was cooled to 590° F. and a relatively large increase in C.R. to 7.73 was then required for an optimum value. The diagrams differ from the C pair in showing that an increased rate of combustion followed the initiation of nuclear ignition at the higher value of Opt.C.R. The temperature of the plug appears to have been reduced to be lower than that of the exhaust valve because Opt.C.R. remained constant as plug temperature was further reduced to 520° F. and then to 420° F. if mixture strength were maintained constant as shown by diagrams not reproduced.

*Mechanical and Gas Vibrations*

Low frequency vibrations which appear in the expansion stroke and extend into the high frequency gas vibrations set up by nuclear ignition are mechanical vibrations of the engine. They were reproduced by holding a small vibrating engraving tool in contact with the outer end of the pressure pickup. The high frequency gas vibrations shown by the A diagrams are confused because pressure rise due to surface ignition began 10° before t.d.c. A single set of high frequency pressure vibrations appears on the B diagrams when plug temperature was reduced by nearly 100° F. and there was a consequent delay in the occurrence of surface ignition. A double set of high frequency pressure waves appear on the D diagrams because they include parts of two cycles which differed slightly in timing.

*Exhaust Valve Temperature and Opt.C.R. as Affected by Mixture Strength*

An experiment with a particular mixture strength was begun with the T.P. uncooled and values were obtained for its temperature and the corresponding Opt.C.R. The T.P. was then cooled to successively lower temperatures and corresponding values for Opt.C.R. determined as described at the beginning of this section. The experiment was continued until a constant value for Opt.C.R. was obtained for successively lower plug temperatures. It was indicated accordingly that the plug temperature had become equal to and then lower than that of the exhaust valve. The temperature of equality could then be determined from a graph for the relation between plug temperature and Opt.C.R. provided great care had been taken to maintain constancy of operating conditions.

Examples of the graphs obtained when mixtures were 7.7% weak, 24% weak, and chemically correct are given by Fig. 3. Graphs obtained when mixtures were 10%, 20%, 56%, and 102.5% rich are given by Fig. 4. It will

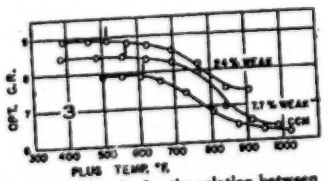


FIG. 3. Graphs for the relation between Opt. C.R. and plug temperature, heptane–air mixtures correct and weaker. The temperature at which that of the plug was the same as the temperature of the exhaust valve is indicated by small arrows.

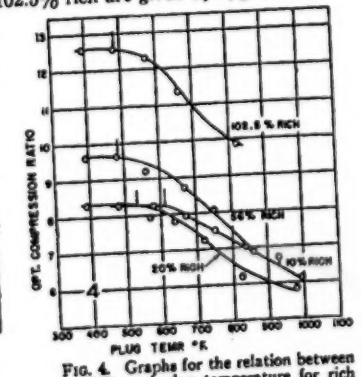


FIG. 4. Graphs for the relation between Opt. C.R. and plug temperature for rich heptane–air mixtures. The temperature at which that of the plug was the same as the temperature of the exhaust valve is indicated by small arrows.



be seen by reference to the graphs that the temperature at which the T.P. ceases to affect the value of Opt.C.R., by becoming equal to that of the exhaust valve, is shown with a fair degree of accuracy by the small arrows on the graphs.

It is of interest that Opt.C.R. tended to become dependent on M.S. only, as that factor was increased to be greater than 20% rich. Thus the temperature of the exhaust valve was 530° F. for a mixture 20% rich. It diminished only to 480° F. for a mixture 56% rich and remained at that temperature as M.S. was increased to be 102% rich.

*The Relation between Opt.C.R. and Plug Temperature for Heptane–Air Mixtures Leaner than 37½% Weak*

The measurement of exhaust valve temperature by the T.P. method is based on a variation of Opt.C.R. with plug temperature when M.S. has particular values, as illustrated by the graphs of Figs. 3 and 4. When however the values of M.S. were less than 37½ weak, a nearly constant value of Opt.C.R. was obtained for a particular value of mixture strength while the temperature of the plug was varied over a wide range. Experimental results obtained for particular values of M.S. ranging from 40.5% weak to 72% weak are given by the graphs of Fig. 5. They afford an explanation for the failure of the T.P.

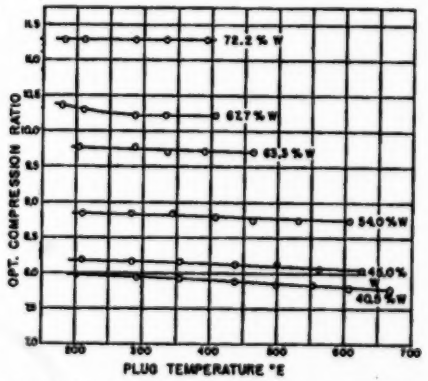


FIG. 5. Graphs showing that the relation between Opt. C.R. and plug temperature remains nearly constant at particular values of mixture strength ranging from 40.5% weak to 72% weak.

method to measure the temperature of the exhaust valve when mixtures were leaner than 37½% weak. The experimental results are of even more interest in showing that for any particular mixture within the range 40.5% weak or weaker, Opt.C.R. remains substantially constant while plug temperature is increased from 200° F. to higher temperatures ranging from 400° F. for a mixture 72% weak to 675° F. for a mixture 40.5% weak. If the plug temperature remained constant at 400° F., Opt.C.R. would vary with M.S. only over the range 40.5% weak to 72% weak.

## III. EXPERIMENTAL RESULTS OBTAINED WHEN THE C.F.R. ENGINE WAS OPERATED WITH IGNITION BY COMPRESSION

Compression ignition experiments described in this Section were carried out over a wide range of heptane–air mixtures, while the temperature of the exhaust valve was measured by the T.P. method and then by a direct thermocouple method. Further experiments were then carried out with the T.P. method used to measure the temperature attained by a sodium cooled exhaust valve. C.R. was always adjusted to an optimum value and corresponding values for I.H.P. and I.T.E. were determined.

*Exhaust Valve Temperature Measured by the T.P. Method; Heptane–Air Mixtures*

The solid C.F.R. exhaust valve used for the experiments, and for those described earlier, was of nichrome steel with a stellite seating. The heptane–air mixtures ranged from 70% weak to 90% rich. The experimental results are given by the graphs of Fig. 6. Significant features are as follows:

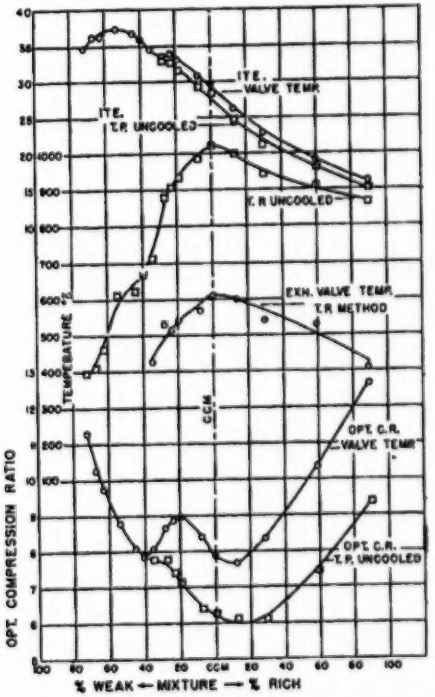


FIG. 6. Graphs for experimental results obtained when the temperature of the standard C.F.R. exhaust valve was determined by the temperature plug method, heptane-air mixtures.



When a correct mixture was used, the uncooled T.P. attained a temperature of 1020° F., the corresponding values for Opt.C.R. and I.T.E. being 6.2 and 27.5% respectively. The temperature of the exhaust valve at the same mixture strength was found to be 610° F. by the indirect T.P. method; the corresponding values for Opt.C.R. and I.T.E. being 7.9 and 29% respectively. The exhaust valve temperature decreased to 440° F. as M.S. was increased from correct to 90% rich, while corresponding values for Opt.C.R. increased to 12.6.

The characteristics of the compression ignition of weak mixtures differed in a striking manner from those for rich mixtures. Thus as M.S. was decreased from the correct value, the temperature of the uncooled T.P. and that of the exhaust valve diminished rapidly and the corresponding value of Opt.C.R. increased in a normal manner until M.S. was 20% weak. Significant events then occurred as M.S. was further reduced to 40% weak. Thus the value for Opt.C.R. diminished from 9.0 to 7.8 instead of increasing, and I.T.E. tended to remain constant at 33½%. The leanest mixture for which the exhaust valve temperature could be determined was 37½% weak and identical values were obtained for Opt.C.R. and I.T.E. when the temperature of the plug was 700° F. and that of the exhaust valve 420° F. The values of Opt.C.R. increased in a normal manner as M.S. was further reduced and the corresponding values for I.T.E. increased to a maximum of 37½% when the mixture became 55% weak, although Opt.C.R. had increased to 8.8 only. The experiment was continued until M.S. was reduced to 72% weak. The I.T.E. had then fallen to 35% and Opt.C.R. had risen to 11.3. The relatively low value of 37½% for maximum I.T.E. was shown by experiments described in Part XXIV (3, p. 240) to be due to the excessive proportion of the heat of the compressed mixture that is lost to the combustion chamber wall when extremely weak mixtures are used at a subnormal charge density in the conditions of the experiments.

*Exhaust Valve Temperature Measured by Thermocouple; Heptane–Air Mixtures*

The drilling of a small hole through the ⅜ in. diameter stem of the C.F.R. nichrome steel exhaust valve in order to provide for thermocouple wires leading to a junction in the valve face was not attempted. The exhaust valve used for the experiments was therefore lathe turned from a bar of cold rolled mild steel. It was a replica of the standard C.F.R. valve except that the stem was made the same diameter as that of the C.F.R. sodium cooled valve, namely 7/16 in. A hole ⅜ in. diameter was drilled through the stem nearly to the valve face and then reduced to 1/16 in. diameter. The ⅜ in. hole was large enough to take iron and constantin wires insulated with fiber glass. The junction was brazed into the 1/16 in. hole to be flush with the face of the valve. The end of the rocker arm which operates the valve was altered to provide a fork through which the thermocouple wires were carried to the temperature indicator. The mild steel valve has been used frequently for more than a year in the low heat load conditions of the experiments without showing any sign of deterioration even on the seating.

The T.P. was replaced by a blank steel plug and the experimental results then obtained are given by the graphs of Fig. 7. It will be noted that a graph

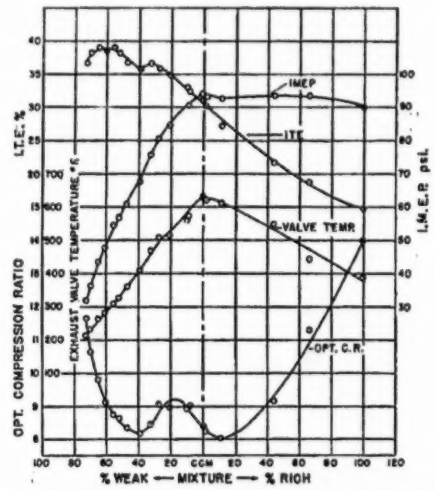


FIG. 7. Graphs for experimental results obtained when the temperature of a mild steel exhaust valve was measured by a thermocouple, heptane–air mixture.

for values obtained for I.M.E.P. is given. Similar I.M.E.P. values were obtained when the T.P. was used but were not shown on Fig. 6, in order to avoid confusion. It will be seen that the relation between Opt.C.R. and I.T.E. was the same as that obtained when the T.P. was used, see Fig. 6, within the limits of experimental error. The graphs for the relation between Opt.C.R. and M.S., Figs. 6 and 7, illustrate the effect of the increase in mixture temperature caused by the extra area of heated surface introduced into the combustion chamber by the T.P. Thus over the mixture range 44% weak to 25% rich, the Opt.C.R. required when the T.P. was used was from 0.1 C.R. to 0.3 C.R. lower than when the exhaust valve temperature was measured by the thermocouple.

The exhaust valve temperatures obtained by the two methods are plotted on a base of mixture strength (Fig. 8). It will be seen that the values fall closely on a single graph. The inconsistencies shown for values of M.S. exceeding 10% rich are not greater than would be expected in view of the irregularity of combustion that occurs in the operation of an engine by compression ignition in the circumstances. The irregularity may be due in part to incomplete vaporization of heptane in rich mixtures with air.

*The Temperature of a Sodium Cooled Exhaust Valve as Measured by the T.P. Method; Heptane–Air Mixtures*

The direct measurement of the temperature of a sodium cooled exhaust valve involves difficult experimental technique. It is a simple matter when the indirect T.P. method can be used. Temperature measurements were made



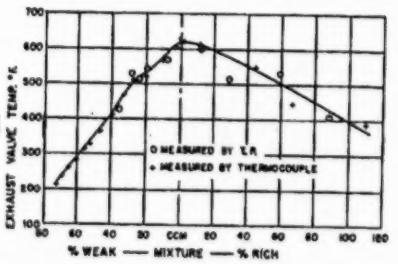


FIG. 8. Graph for a comparison of exhaust valve temperature as measured by the direct and indirect methods.

accordingly when a sodium cooled exhaust valve was fitted in the C.F.R. engine. The valve was of the type in which the hole drilled through the oversize stem extends into the head nearly to the crown. This type was used for hydrogen engine experiments and its design is illustrated by Fig. 15 of Part XXVII (7).

The results of experiments carried out with heptane–air mixtures ranging from 72% weak to 90% rich are given by the graphs of Fig. 9, which include a broken line graph for the temperature of the standard C.F.R. exhaust valve taken from Fig. 6.

It will be seen by reference to the relevant graphs that the temperature attained by the sodium cooled valve was the lower by 290° F. when the mixture was correct. Its temperature diminished more slowly than that of the solid valve as M.S. was increased and Opt.C.R. raised as required. This is attributed to the sodium cooling remaining effective, because I.M.E.P. and the consequent heat load remained nearly constant as shown earlier by Fig. 7.

I.M.E.P. and heat load decreased rapidly as M.S. was reduced from correct, with the result that the length of valve stem enclosed by the guide approached the temperature of solidification of the sodium and the rate of heat transfer from the head of the valve to the relatively cool guide was reduced. Thus the temperature of the sodium cooled valve was 100° F. only lower than that of the solid valve when mixtures ranged from 30% weak to the 40% weak at which the T.P. method of measurement became ineffective. Nevertheless the sodium cooled valve would continue to attain the lower temperature when still weaker mixtures were used even if the sodium solidified, because of its larger stem diameter.

The most significant effect shown to be due to a change from the solid to the sodium cooled valve was the consequent change in the combination of mixture strength and Opt.C.R. required for the initiation of nuclear ignition, as shown by the graphs of Fig. 9, which include a broken line graph for the temperatures attained by the C.F.R. standard solid exhaust valve. It will be seen that higher values for Opt.C.R. were required for mixtures ranging from 40% weak to 50% rich when the valve was sodium cooled. The maximum

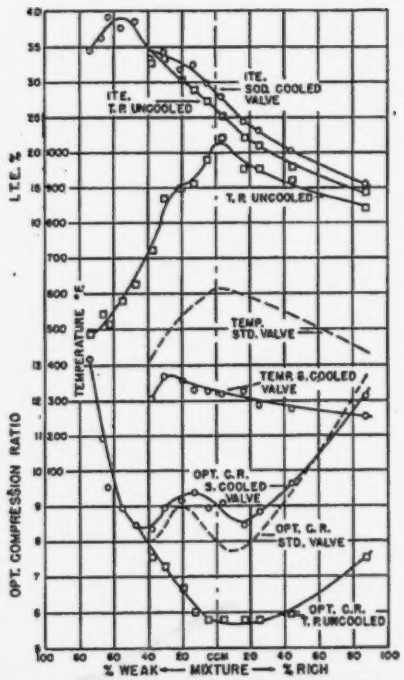


FIG. 9. Graphs for experimental results obtained when the temperature of a sodium cooled exhaust valve was determined by the temperature plug method, heptane–air mixtures.

difference occurred when the mixture was correct. Opt.C.R. was then 7.9 when the solid valve was used and 9.0 after a change was made to the sodium cooled valve.

The value of 28% was obtained for I.T.E. when the solid exhaust valve was used and the Opt.C.R. was 7.9 (see Fig. 6). When a change was made to the sodium cooled valve I.T.E. decreased to 27% although Opt.C.R. was higher at 9.0. The reduction of exhaust valve temperature by 290° F. at correct mixture, caused by sodium cooling, would be accompanied by a reduction in the temperature of the mixture at the end of compression. The observed increase in Opt.C.R. to 9.0 is regarded as having been required for the formation of an igniting concentration of nuclei in the cooler mixture.

## IV. FLAME COLOR, LUBRICATING OIL EFFECT, KNOCK INTENSITY, COLD STARTING

### *Flame Color*

A short length of polished Pyrex rod was used as a window. It was set in a mild steel mounting adapted to replace an 18 mm. spark plug in the cylinder



wall. The inner end of the Pyrex rod was set ¼ in. back from the cylinder wall and consequently tended to remain clean. Flame color was observed as mixture strength was increased from 75% weak to 100% rich. Compression ratio was always adjusted to the value required for maximum power output.

*Mixture 75% to 40% Weak*

The color was a brilliant light blue which became tinged with purple as M.S. was increased. The light intensity, as measured by a photomultiplier, was feeble.

*Mixture 41% to 39% Weak*

In this narrow range the purple tinge of the blue flame was replaced by white with a consequent marked increase in light intensity.

*Mixture 39% Weak to 35% Rich*

The flame was a brilliant white with an occasional tinge of yellow. Light intensity was so great that visual observations of the flame were necessarily brief.

*Mixture 25% to 100% Rich*

The brilliant white tended to pink as M.S. was increased to 30% rich. The color then changed to a bright orange as M.S. was further increased to 35% rich. The orange color persisted as M.S. was increased to be 100% rich. Light intensity diminished as color changed from white to pink and then to orange.

### *Effect of the Combustion of Lubricating Oil*

It was shown by the hydrogen engine experiments described in Part XXVII (7) that the decomposition of lubricating oil *vapor* provided carbon nuclei which ignited the mixture with air before completion of the compression stroke. These experiments were carried out at engine speeds rising to 1800 r.p.m. and with normal charge density. Even so, an igniting effect arising from the lubricating oil did not occur until C.R. was raised to 12:1 and the rate of oil passing the piston increased because the top piston ring overlapped the three spark plug holes in the cylinder wall. Enough oil was then vaporized for the production of an igniting concentration of carbon nuclei.

The reactions required for the provision of nuclei of ignition by the vapor of lubricating oil would not be expected in the conditions of low heat load used for the experiments of this Part, and no evidence of such an effect was discerned. Lubricating oil passing the piston was necessarily burnt, at least in part, during combustion of the heptane, especially when air was in excess of that required for a correct mixture. Thus the flame color of heptane–air mixtures leaner than 41% weak was fundamentally a bright blue. The bright flashes of flame ranging in color from orange to white that were then observed appeared to be directly in front of the viewing window, not in the body of the mixture. They were attributed to combustion of the spray of oil thrown up from the periphery of the piston as its direction of motion reversed at t.d.c. It is possible that these bright flashes persisted as mixture strength was increased but were obscured by the intense white light emitted by the burning

carbon nuclei regarded as being responsible for the detonation of heptane–air mixtures richer than approximately 25% weak.

*Combustion Knock*

The combustion of mixtures leaner than 40% weak that occurred after nuclear ignition was notably silent. As the mixture was enriched, combustion knock increased slowly in intensity until the mixture was 25% weak. Intensity then increased rapidly to become severe at correct mixture. Little change in intensity occurred as M.S. was increased to be 80% rich. Knock intensity diminished slowly as M.S. was further increased.

*Cold Starting*

A mixture leaner than 40% weak was always used for cold starting. Ignition occurred immediately on raising C.R. to from one to two units higher than the optimum value used for continuous running. The C.R. was then lowered as the engine warmed up and adjusted to the value required for maximum power output for the measured mixture strength.

## DISCUSSION

It is of interest to compare the experimental results of this Part with those obtained by others when combustible gaseous mixtures were ignited by rapid compression in a single stroke compression ignition machine and ignition temperature calculated according to the familiar equation,

$$[1] \qquad T_1/T_0 = (P_1/P_0)^{1-1/\gamma} = (V_0/V_1)^{\gamma-1}.$$

Tizard in a paper on the causes of detonation in the end gas in a spark ignition engine (11) described experiments with heptane–air mixtures as carried out with a single stroke compression ignition machine made by Ricardo. The design of the machine is illustrated in the reference quoted. Both the volume and pressure ratios were observed. Thus an apparent value for $\gamma$ was calculated from the second and third terms of equation [1], which allowed for loss of heat to the cylinder wall during compression and for the concentration of heptane vapor in the mixture with air. The value of $\gamma$ calculated for a correct mixture was 1.31. It increased to 1.33 for a fuel to air ratio of 0.027 and decreased to 1.22 for a fuel to air ratio of 3.75. These apparent values for $\gamma$ were obtained when the "delay period" preceding detonation was not maintained at a fixed value. The ignition temperature calculated accordingly varied ±8° C. only, from an average value of 291° C. (555° F.). The delay period was taken as the time interval between the completion of compression and the sharp pressure rise caused by detonation. It is probable that if the compression ratios at which ignition occurred had been as required for a constant delay period, the calculated ignition temperature would have had even a more nearly constant value, over the M.S. range of the experiments.

*The Effect of Surface Temperature on the Compression Ratio Required for Ignition*

It was found by Tizard that the compression ignition temperature of heptane–air mixtures was nearly constant irrespective of the concentration of heptane but that the C.R. ratio required for the igniting effect varied with the concentration and the delay period. When, however, ignition is by compression in an engine, the temperatures attained by surfaces in the combustion chamber have an important influence on the compression ratio required for the initiation of an igniting effect. The relation between surface temperatures in the combustion chamber of the C.F.R. engine and the occurrence of ignition at optimum values of the compression ratio was obtained by means of the temperature plug used for the experiments of this Part. Noteworthy features of the experimental results as exhibited by the graphs of Fig. 9 are stated below.



When the heptane–air mixture was correct and the plug not cooled, its temperature rose to 1020° F. when the Opt.C.R. was 5.7. The rate of oxidation on the surface of the plug sufficed to start a flame but a transition to nuclear ignition was necessary in order that maximum combustion pressure could occur at the time required for maximum power output as shown by the A indicator diagrams of Fig. 2.

When the plug was cooled to 610° F. to be equal to the temperature of the standard C.F.R. exhaust valve, the Opt.C.R. was 8.0. Then when it was cooled to 325° F. to be equal to the temperature of the sodium cooled exhaust valve, the Opt.C.R. was 9.0. Surface oxidation was not eliminated in either case, but the rate was too low to start ignition; the change in rates was indicated by changes in the length of the fillet which connected compression and combustion pressures.

It is shown by the graphs of Fig. 9 that when M.S. was reduced to be 40% weak, the value of Opt.C.R. remained at 8.0 while the plug temperature was 700° F. or reduced to 400° F. to be equal to that of the standard C.F.R. exhaust valve. At leaner mixtures, Opt.C.R. increased nearly in direct proportion to the decrease in M.S. The temperature attained by the uncooled plug was always higher than that of the exhaust valve as shown by the graphs of Figs. 6 and 7. The difference decreased as M.S. decreased but even with a mixture approximately 75% weak, the plug temperature was 400° F. (Fig. 6) and that of the exhaust valve 200° F. (Fig. 7). When a mixture was 40.5% weak or leaner, Opt.C.R. remained nearly constant as the temperature attained by the plug for a particular mixture was reduced by cooling to a value as low as 200° F., as shown by the graphs of Fig. 5.

Data determined for the relation between plug temperature and Opt.C.R. when the exhaust valve was sodium cooled have been used to obtain the relation between Opt.C.R. and M.S. if the plug temperature were held constant at a temperature of 400° F., which is 40° F. higher than the maximum attained by the valve as shown by the relevant graphs of Fig. 10. The temperature of the valve could not be measured by the T.P. method when the mixture was leaner than approximately 38%, as was the case when the exhaust valve was not cooled.

It will be seen by reference to Fig. 10 that the graphs for the relation between Opt.C.R. and M.S. nearly coincided when mixtures were 39% to 30% weak. A real separation became apparent as M.S. was increased, and with a correct mixture, Opt.C.R. was 8.9 with the sodium cooled valve at a temperature of

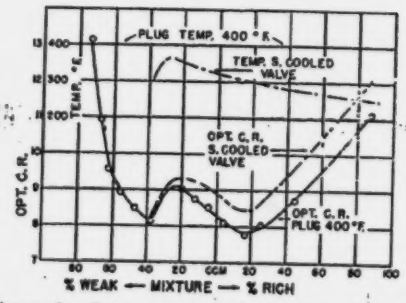


FIG. 10. Solid line graphs—Opt. compression ratios for compression ignition of heptane–air mixtures 72% weak to 90% rich when plug temperature is always 400°F. and the exhaust valve is sodium cooled.

320° F., and 8.3 with the T.P. at a temperature of 400° F. The differences increased as M.S. was increased and with a mixture 80% rich Opt.C.R. was 11.7 for the sodium cooled valve, which then attained a temperature of 260° F., and 10.7 for the temperature plug at a temperature 140° F. higher.

The relatively low heat load in the conditions of the experiments made it possible to show that the *decrease* in Opt.C.R. as M.S. was reduced over the range 25% to 40% weak is a property of a "detonating" fuel. When a nondetonating fuel such as benzene was used in the same conditions and spark timing always adjusted to the optimum value, the corresponding Opt.C.R. *increased* as M.S. was decreased from approximately correct to 40% weak, but ignition by either spark or compression did not occur at leaner mixtures.

### *The Relation Between the Time of Compression and the Compression Ratio Required for the Explosive Ignition of Correct Heptane–Air Mixtures*

The relation is given in Table I as obtained by Tizard when using the Ricardo compression ignition machine, by Taylor *et al.* when using the machine developed in the Massachusetts Institute of Technology (10), and by the C.F.R. engine experiments of this Part when carried out with the standard uncooled exhaust valve, valve timing being taken into account.

Explosive ignition was initiated in Tizard's experiments after a "delay

TABLE I

| | Initial pressure | Initial temperature, °F. | Time of compression, sec. | C.R. |
|---|---|---|---|---|
| Tizard | Atmos. | 140° | 0.0625 | 6.3 |
| Taylor *et al.* | Atmos. | 150° | 0.006 | 12.3 |
| C.F.R. engine | 53% atmos. | 100° | 0.061 | 7.9 |



period" of 0.25 sec. as reckoned from the completion of compression. That is, the time was three times the time of compression. The delay was 0.001 sec. approximately in the Taylor *et al.* experiments, that is, $\frac{1}{8}$ of the time of compression. Explosive ignition was initiated in the engine at approximately 5° of crank revolution after t.d.c., as shown clearly by experiments made when the T.P. was not used, Part XXI (6, Fig. 5) and Part XXV (4, Fig. 7). The delay time if reckoned from the completion of compression at t.d.c. was then 0.002 sec., which is 1/30 of the time of compression although Opt.C.R. was 7.9 only. The delay time must therefore have begun during the compression stroke of the engine.

The true delay time is that required for preflame reactions to produce an igniting concentration of carbon nuclei in the gaseous mixture according to the nuclear theory as stated in Part IV (1). This statement was made in respect of the end gas in a spark ignition engine and applies only to gaseous mixtures that can thus be ignited. It is well known that spark ignition is irregular in the mixture range 20% to 25% weak. It was shown to become completely ineffective as M.S. approached 40% weak, Part XXI (6, p. 235). Further discussion will for the present be restricted accordingly.

Oxidation and decomposition reactions can occur simultaneously during compression in a carburetor engine operated as for the experiments described in this Part. It is shown by the indicator diagrams of Fig. 2 that as the plug temperature was reduced to that of the exhaust valve, the oxidation reaction on the combined surface area of the plug and valve was effective only in providing a fillet connecting compression and explosion pressures. The explosive ignition must therefore have been due to the carbon nuclei produced by a decomposition reaction. The rate of the production of carbon nuclei increases with the increase of temperature and pressure due to an increase of C.R. The concentration of nuclei per unit volume of gases mixture increases directly with increase of pressure. An explanation may thus be provided for the delay time of approximately 0.001 sec. observed by Taylor *et al.* for a correct heptane–air mixture and a C.R. of 12.3. It is possible, however, that the delay time began before compression had been completed, in view of the fact that compression time was six times that of the delay time as it was measured.

### *Explosive Ignition of the End Gas when Ignition is by Spark*

When ignition is started by a spark or by a hot spot provided by a surface in the combustion chamber of an engine, flame is propagated in the compressed fuel–air mixture by the normal thermal process unless explosive ignition occurs in the mixture ahead of the flame front. The phenomenon is commonly described as detonation of the end gas and was observed in the experiments of this Part when a nearly correct heptane–air mixture was ignited by a hot spot provided by the temperature plug, as shown by the A indicator diagrams of Fig. 2. A similar effect was demonstrated by Taylor *et al.* when a heptane–air mixture compressed in the M.I.T. machine was ignited by a spark (10, Fig. 68).

Relevant data for the two experiments are tabulated below.

TABLE II

| Method of experiment | F/A ratio | C.R. | Ignition | Approx. time of combustion of end gas |
|---|---|---|---|---|
| M.I.T. machine | 0.060 | 6.8 | Spark | 0.3 millisec. |
| C.F.R. engine | 0.064 | 6.77 | Hot spot | 0.8 millisec. |

The combustion times were taken from pressure time diagrams and although the values are approximate, the longer time required for combustion of the end gas in the engine is consistent with its dilution with residual products to a greater than normal extent because the initial pressure was 53% of atmospheric. It is also to be noted that initial pressure in the M.I.T. machine was 5.5% greater than atmospheric and the mixture 3% richer than that in the engine.

The high speed photographic records taken in the course of experiments with the M.I.T. compression ignition machine show that ignition was initiated by discrete bright spots of flame. Taylor *et al.* comment on the similar bright spots observed by C. D. Miller when high speed photographs were taken of the autoignition of the end gas in an engine (9, pp. 98–143) and further on the theory of King *et al.* that nuclei of free carbon are involved in the autoignition process as shown by experiments with the hydrogen engine described in Part V (8). The theory received further support by the hydrogen engine experiments described later (in Part XXVII (7)).

It should be noted that the bright spots mentioned by Taylor *et al.* appeared prior to autoignition. The phenomenon was therefore not similar to that observed by Miller when autoignition occurred in the end gas of an engine. The bright spots which appeared in the M.I.T. experiments may well have indicated the beginning of ignition on the surface of the glass plate which was necessary for the taking of photographic records of the progress of combustion.

*Detonation Pressure Waves*

The temperature of a homogenous gaseous fuel – air mixture is not uniform at the end of compression even in a single stroke compression ignition machine, as mentioned by Tizard and later by Taylor *et al.* An even greater lack of uniformity would be expected in an engine because of the local heating effect of the exhaust valve. The decomposition or pyrolysis of the fuel to the extent necessary for the production of an igniting concentration of nuclei would be most advanced in the portion of the mixture in which temperature exceeded the mean value due to compression to the greatest extent. It may safely be assumed that maximum compression temperature was attained by the mixture near the exhaust valve irrespective of turbulence, when ignition was by compression as in the experiments described in this Part. When ignition is by spark the position of maximum temperature in the end gas is difficult to define because it depends on the position of the spark plug relative to that of the exhaust valve, on the characteristics of turbulence, and on the geometry of the combustion space.



Detonation in any event would occur in only that part of the mixture is sensitive to the effect. That would be the mixture in the end gas in a ignition engine and the whole mixture at the end of the compression in a compression ignition engine. The consequent pressure wave as it through the remainder of the mixture would raise its somewhat lower tem ture to the degree required to start additional pressure waves. There thus be a complication of pressure waves which would be increased b flections from the walls of the combustion chamber and by the impact wave upon another. It is not surprising therefore that no demarcation detonation wave was shown by the flame photographs of Taylor *et al.* alth they were taken at the rate of 10 frames per millisecond or by the re pressure change diagrams taken in the course of experiments described in Part. However in all of these diagrams the gas vibrations which followed nation were shown clearly although their frequency as measured from enl ments was 5.0 per millisecond approximately.

*Nuclei of Ignition*

Detonation that occurs in the end gas when fuel–air mixtures are ig by spark is, in accordance with the nuclear theory of ignition as stat Part IV (1), due to the igniting effect of finely divided carbon derived decomposition or pyrolysis of the fuel. This carbon accounts for the bril white flame of detonating combustion. The flame is blue in operating cond in which detonation does not occur unless the mixture is over rich and va ization is not complete. Carbon not consumed in the flame appears as a re on surfaces in the combustion chamber and as black smoke in the exhau

When a spark plug was not used, as for the experiments with heptan mixtures described in this Part, and C.R. was raised to the value require ignition with maximum power output, detonation began in part of the w gaseous mixture, as there was then no end gas. The characteristics of nating combustion were similar to those described for spark ignition whe with spark ignition, mixtures were richer than 25% weak.

Mixture strength appears to have a critical value when it is 25% w Then as it is increased from that value, residues of finely divided carbon t to appear on surfaces in the combustion chamber when detonation foll spark or compression ignition. As M.S. decreases from 25% weak, sp ignition tends to become of nil effect. Ignition by compression remains effec but residues of the nuclei of ignition appear to be a mixture of carbon and re A corresponding increase in the inflammability of the nuclei of ignition indicated by a decrease in optimum C.R. as mixture strength was redu from 25% to 40% weak. Then as mixture strength was further reduced flame of combustion ceased to be white and became a brilliant blue.

Aldehydes were noticeable in the exhaust as the mixture became leaner th 25% weak. The accompanying increase in the inflammability of carbon nu may be due to their absorption and condensation of a particular variety aldehyde. However, residues of resinous substance increased in quantity wh rate of aldehyde formation increased as mixtures leaner than 40% weak w

used, as described in Part XXIV (3, p. 235). Corresponding values of Opt.C.R. increased and flame became a bright blue. This indicated that nuclei of ignition no longer contained carbon. The combustion of these lean mixtures occurred in two stages and was nearly silent.

Experiments carried out especially to determine the role of aldehydes in the compression ignition of mixture leaner than can be ignited by a spark will be described in the second paper on the subject of this Part.

## ACKNOWLEDGMENTS

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